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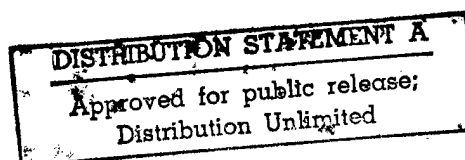
DESP

October 1998

**STUDY OF SPECIES PRODUCED BY ATOMIC OXYGEN
IMPACT ON POLYMER-RESIN MATERIALS USING
A MASS SPECTROMETRY METHOD**

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1 INTRODUCTION

Oxygen atoms in Low Earth Orbit at altitudes between 200 and 900 km, combined with high orbital velocities, give rise to hyperthermal reactions on satellite surfaces. Spacecraft material surfaces are degraded by these hyperthermal oxygen atoms upon impact : polymer suffers weight loss, change in various properties, loss of surface gloss, and premature aging. Erosion of surface materials by fast O-atoms is accompanied by emission of volatile reaction products. These constitute a possible source of contamination for critical parts of spacecraft onto which they can condense.

The objective of the present work is to measure the yield (molecules per incident beam particle) of volatile species (specifically CO and CO₂) produced by atomic oxygen (AO) bombarding a polymer-resin (polysulfone) target, and to measure the corresponding velocity spectra.

This study is performed in CASOAR, a space simulation chamber employing a laser-assisted source of fast oxygen atoms. A quadrupole mass spectrometer (QMS) is used either to characterize the fast atomic oxygen pulsed beam or to analyze the species evolved by the surface of the polymer-resin target.

2 ATOMIC OXYGEN SOURCE

2.1 Introduction

The atomic oxygen source used in CASOAR involves a pulsed laser-induced breakdown (PLIB) of molecular oxygen. This technique, described in [1], delivers a pulsed beam at 8 km/s, with a typical fluence of 3×10^{15} atoms/cm² per shot at 40 cm from the source. A study of the beam [2], performed in 1996, by quadrupole mass spectrometry, shows that atomic oxygen beam delivered by CASOAR contains fast neutral and ions. The beam composition obtained is reported in table a. Ultraviolet (UV) and vacuum ultraviolet (VUV) photons with wavelengths down to 60 nm are also produced during the initial oxygen plasma formation within the nozzle.

| Specie | Velocity (km.s ⁻¹) | Fluence per pulse (species.cm ⁻²) | Relative quantity |
|-----------------------------|--------------------------------|---|-------------------|
| O | 8 ± 15% | 2.9×10 ¹⁵ | 91% |
| O ₂ | 8 ± 15% | 2.6×10 ¹⁴ | 9% |
| O ⁺ | 10.6 ± 15% | 7.9×10 ¹⁰ | 25 ppm |
| O ₂ ⁺ | 10.9 ± 15% | 1.4×10 ¹⁰ | 5 ppm |

Table a : Different species in the atomic oxygen pulsed beam at 8 km.s⁻¹ velocity.

2.2 Mass spectrometry – Characterization of the beam

The experimental apparatus allowing the characterization of the beam is shown on figure 1. It uses a quadrupole mass spectrometer located 100 cm from the nozzle and whose optical axis with the CO₂ Laser beam forms an angle of 8 deg. The quadrupole mass spectrometer includes a ionization chamber where neutral species are ionized by crossed-beam electron impact. After formation, ions are transferred to the quadrupole. After transmission through the quadrupole, the ions are electrically detected, either by a Faraday cup or by the secondary-electrons multiplier (SEM).

The signal given by the detectors are obtained on an oscilloscope and give the Time-of-flight distribution of the filtered species between their formation in the nozzle and their detection by the SEM.

Figure 2 gives the final result of this characterization with time-of-flight distribution of the species constituting the beam.

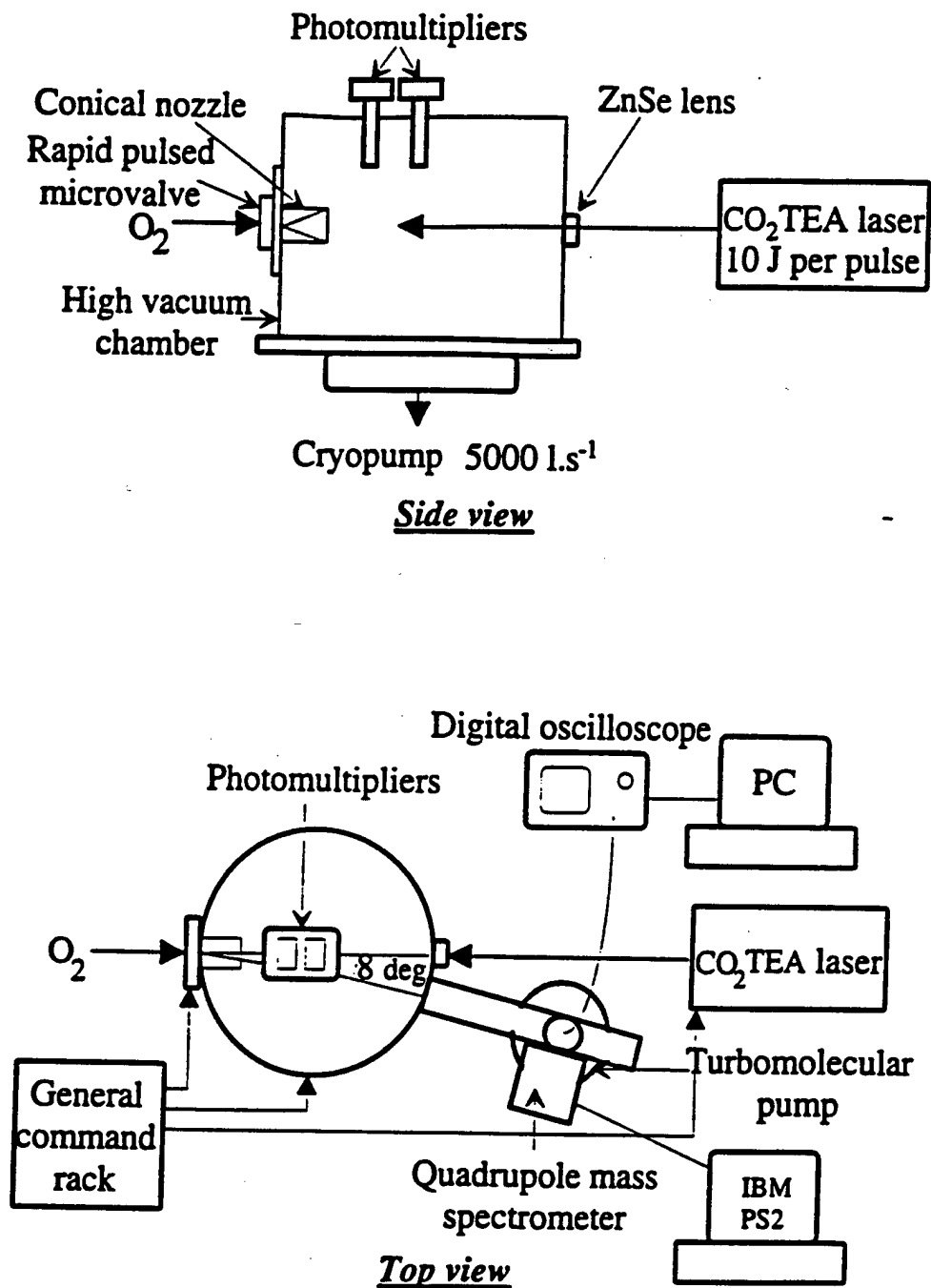


Figure 1 : Experimental set-up for the characterization of the beam.

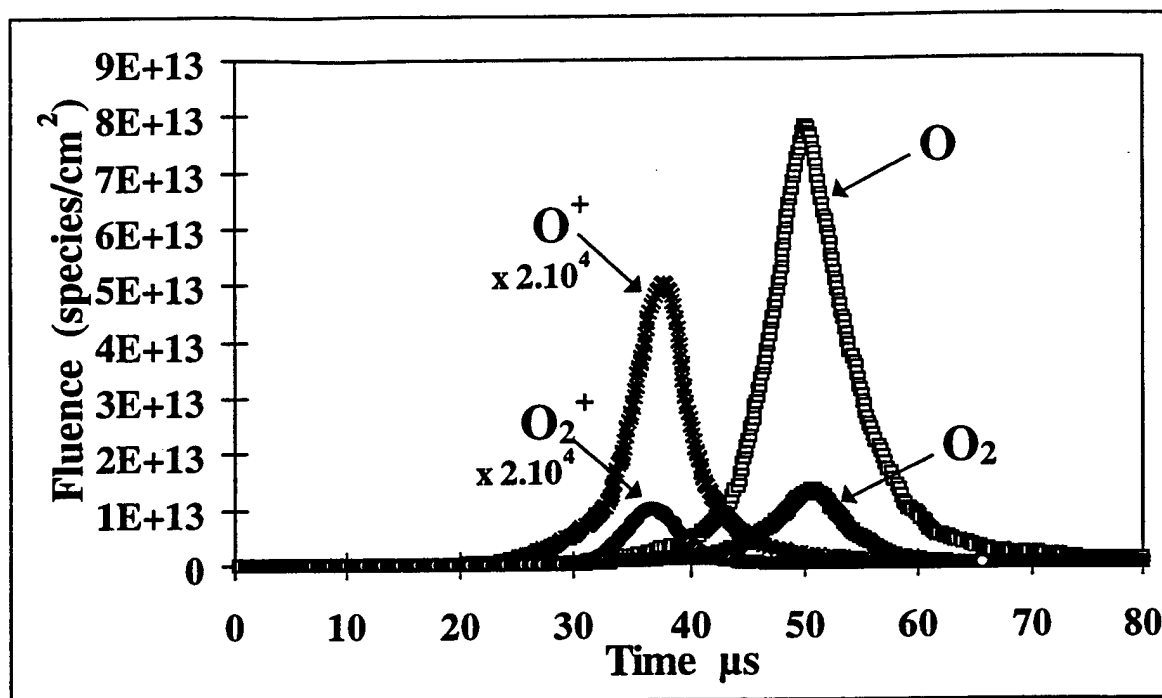


Figure 2 : Distribution of beam species at 40 cm from the nozzle.

2.3 Measurement of the velocity of the beam by photomultipliers :

As it is shown in Figure 1, two photomultipliers (PM) are used to follow excited species. Desexciting from the level $3p^5$ to $3s^5$, the excited atoms emit photons with 777 nm of wavelength, that both PM can detect. The distance between the PM being 7.2 cm, the TOF of the species can give their velocity.

Figure 3 gives an example of the measurements of the photomultipliers corresponding to a beam velocity of 8.2 km/s.

3 MASS SPECTROMETRY – REACTION PRODUCTS ANALYSIS

Figure 4 shows the experimental set-up for the study of species evolved by the target. After ionization the oxidation products are introduced in the quadrupole mass spectrometer, by means of a collection and transfer ion optics. As before, an oscilloscope is used to visualize the time-of-flight distributions of each specie.

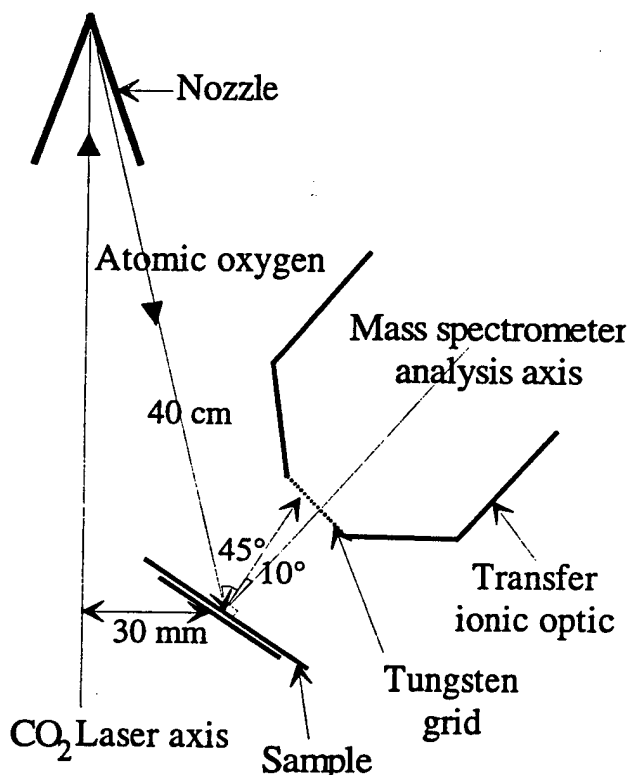


Figure 4 : Sample exposure to O-atom beam in CASOAR

Preliminary, experiments have been carried out in this facility. Mass spectra of reaction products of fast oxygen atoms-materials interaction have been measured during initial studies on some polymeric samples; they have been reported in [3].

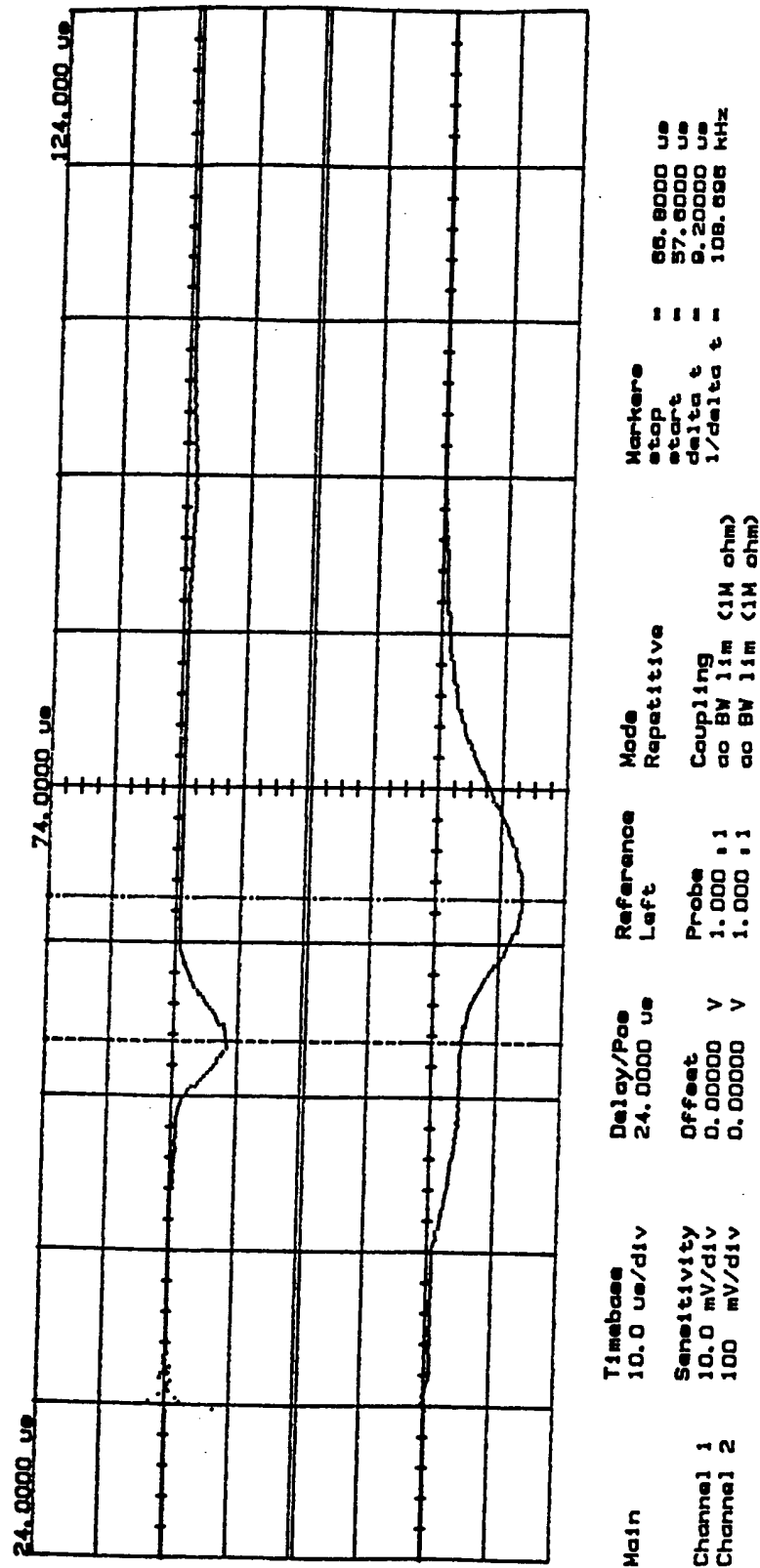


Figure 3 :Signals measured by the photomultipliers.

4 SAMPLES :

The samples were provided by EOARD.

They were constituted by a piece of polysulfone material of 1 cm² mounted on a conductive sample holder slightly larger.

A large piece of polysulfone was also provided to DESP and used for several experiments as it will be explained later.

5 MATERIAL TEST PROCEDURE

The sample studied under the pulsed beam of CASOAR is mounted in front of ion optics and the rear face (metallic) is biased at a positive voltage. The ionized products emanating from the sample are introduced into the quadrupole mass filter, via the ion optics, owing to the extraction electric field. The products analysis is carried out in two steps. First, a fast mass scanning is performed. A ratio m/q is taken as a reference (typically $m/q = 44$) and the parameters of the mass spectrometer and the ion optics are adjusted to maximize the signal measured on the oscilloscope. Parameters thus obtained are kept constant for all masses, in order to permit relative quantitative analysis of the different products.

Mass spectrum of oxidation products has been determined, under bombardment by the CASOAR raw beam, composed of all fast neutral and charged species, plus UV-VUV photons emitted by the source; in this configuration, the reaction products are ionized by charge transfer with the charged species.

Another objective of this study was to determine oxidation products mass spectrum under a neutral beam, cleared out by removal of its charged species. In this configuration, the reaction products cannot be ionized by charge transfer but should be ionized by non-resonant multiphoton laser absorption. This configuration was not successful because of problems to synchronize the different elements of the experiment. Nevertheless, the measurement of the time-of-flight and the knowledge of the different velocities of each specie of the beam allowed us to determine the respective influences of ionized and neutral species constituting the beam.

Residual gas molecules present in the simulation chamber, as well as absorbed molecules on the edge of the sample holder, on stainless walls of the ion optics and

the chamber, can be added to the reaction products. In order to deduce such a background noise, product analysis is carried out turning the sample holder facing the atomic oxygen beam.

6 EXPERIMENTS

6.1 Interaction of the raw beam of CASOAR with polysulfone :

6.1.1 Example :

Figure 5 shows the general form of the signals obtained on the sample holder and on the polysulfone target at a mass/charge ratio $m/q = 44$ (CO_2^+).

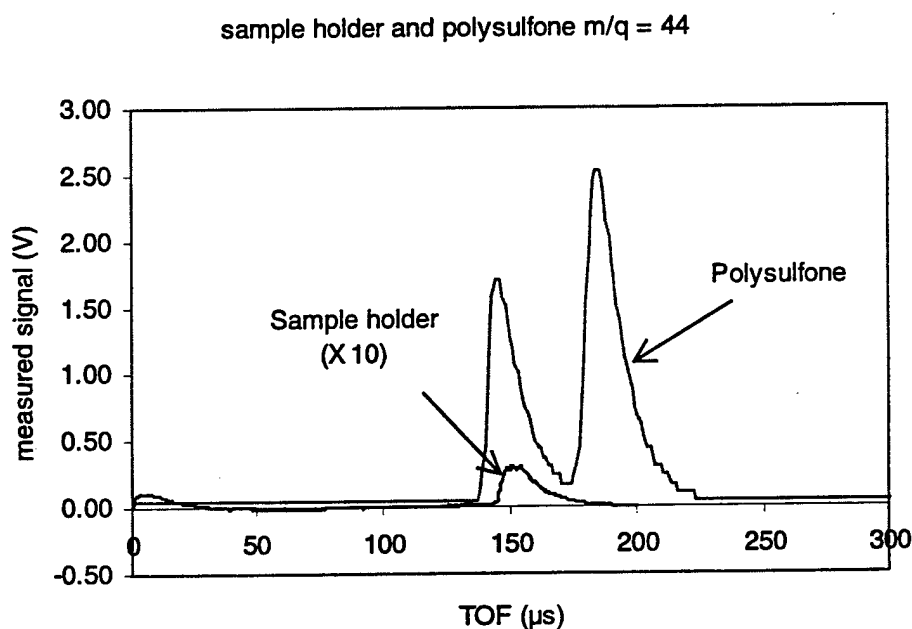


Figure 5 : Signal measured on sample holder and on the polysulfone target for a mass/charge ratio $m/q = 44$ (CO_2^+).

On this figure, the signal measured on the sample holder was multiplied by ten to be legible. The origin of the time axis corresponds to the laser firing, creating the oxygen beam in the nozzle. The time appearance of these peaks can be decomposed in 2 parts :

- Time of flight of the beam species from the nozzle to the sample, located at 40 cm from the nozzle throat.
- Time-of-flight of the reaction products from the sample surface to the secondary electrons multiplier (SEM) through the transfer ion optics and the mass filter.

As the ionized products have the same kinetic energy at the exit of the extracting field, their TOF to the SEM is the same. So, the two distinct peaks are due to the difference in the TOF of the CASOAR beam components responsible for the creation of these products. The first peak is due to the fastest species contained in the beam, i.e. the ions O^+ and O_2^+ . Their velocity is around 13 km/s, compared with the neutral species (O et O_2) travelling at 8 km/s.

By integrating separately the two peaks, distinct mass spectra due to the action of oxygen ions and oxygen atoms can be obtained.

6.1.2 Complete spectra :

Figure 6 shows the spectrum obtained on the sample holder (rear face of the sample facing the beam).

It was observed that between 0 and 16 a.m.u., filtering with the quadrupole was disturbed by the too important quantities of hydrogen and oxygen present in the chamber. It was not possible to solve this problem by rising the mass resolution to a maximum, because this considerably reduced the sensitivity for heavy mass products. Therefore, information related to species with mass lower than 16 will not be presented on the following graphs.

On this figure, we can observe that there is not only gas molecules present in the chamber which are detected but also molecules adsorbed on surfaces. This experiment has been performed after exposition of polysulfone and we can detect the presence of sulfured molecules probably on the metallic surfaces of the experimental system.

Background

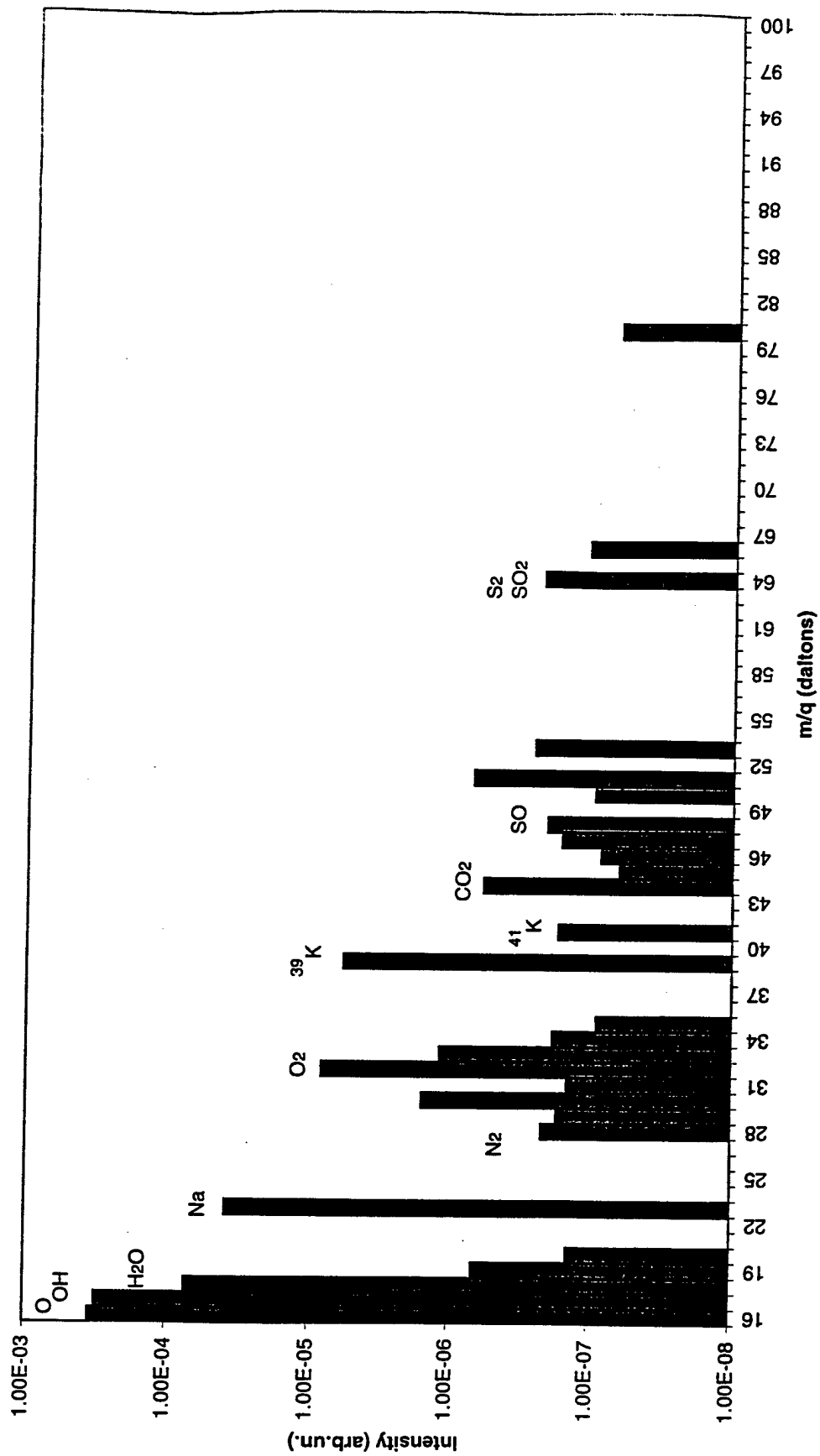


Figure 6 : Mass spectrum measured on the sample holder.

Effect of ions and UV-VUV of the beam on polysulfone

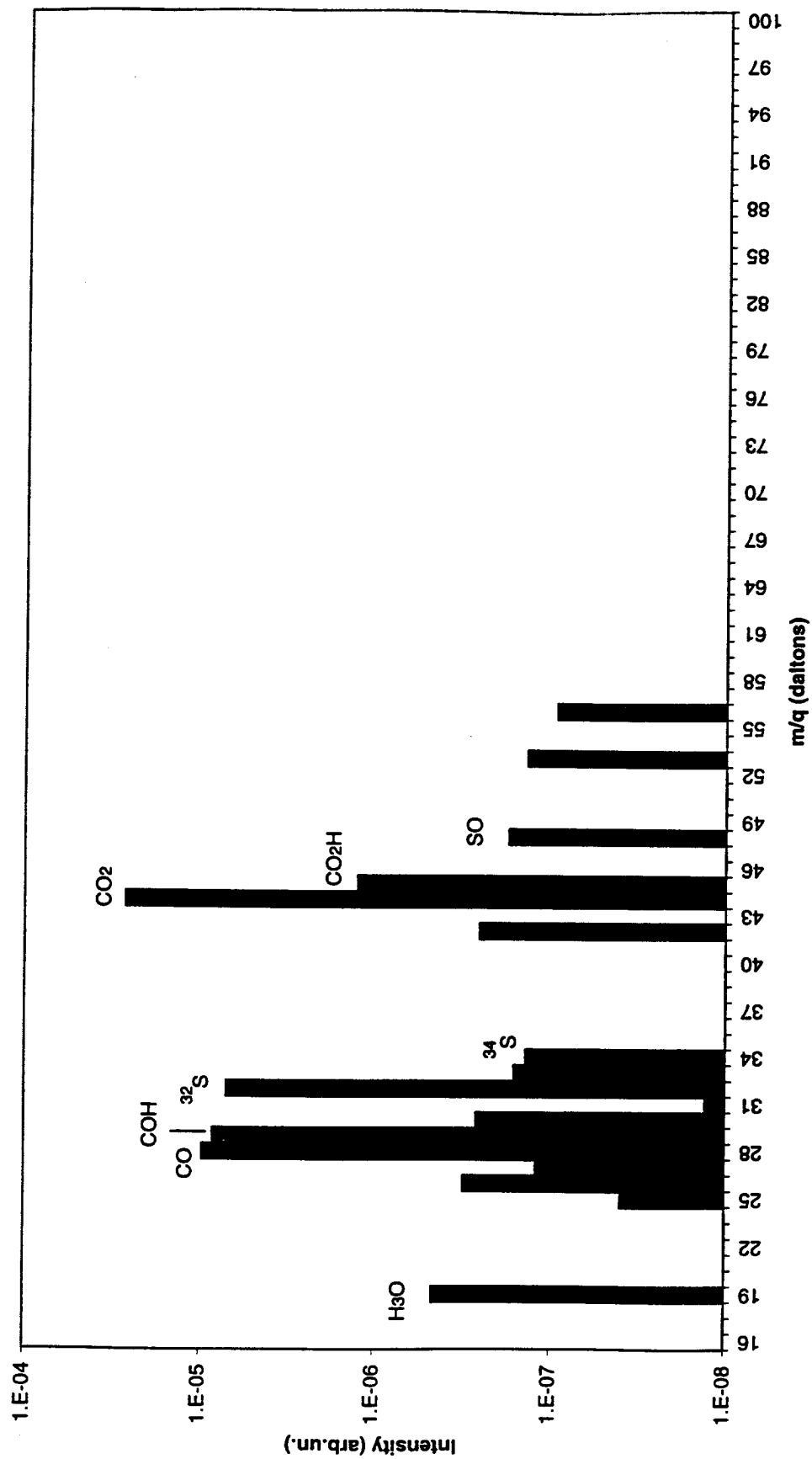


Figure 7 : Mass spectrum measured on the polysulfone. Effect of the ions.

Effect of neutrals on polysulfone

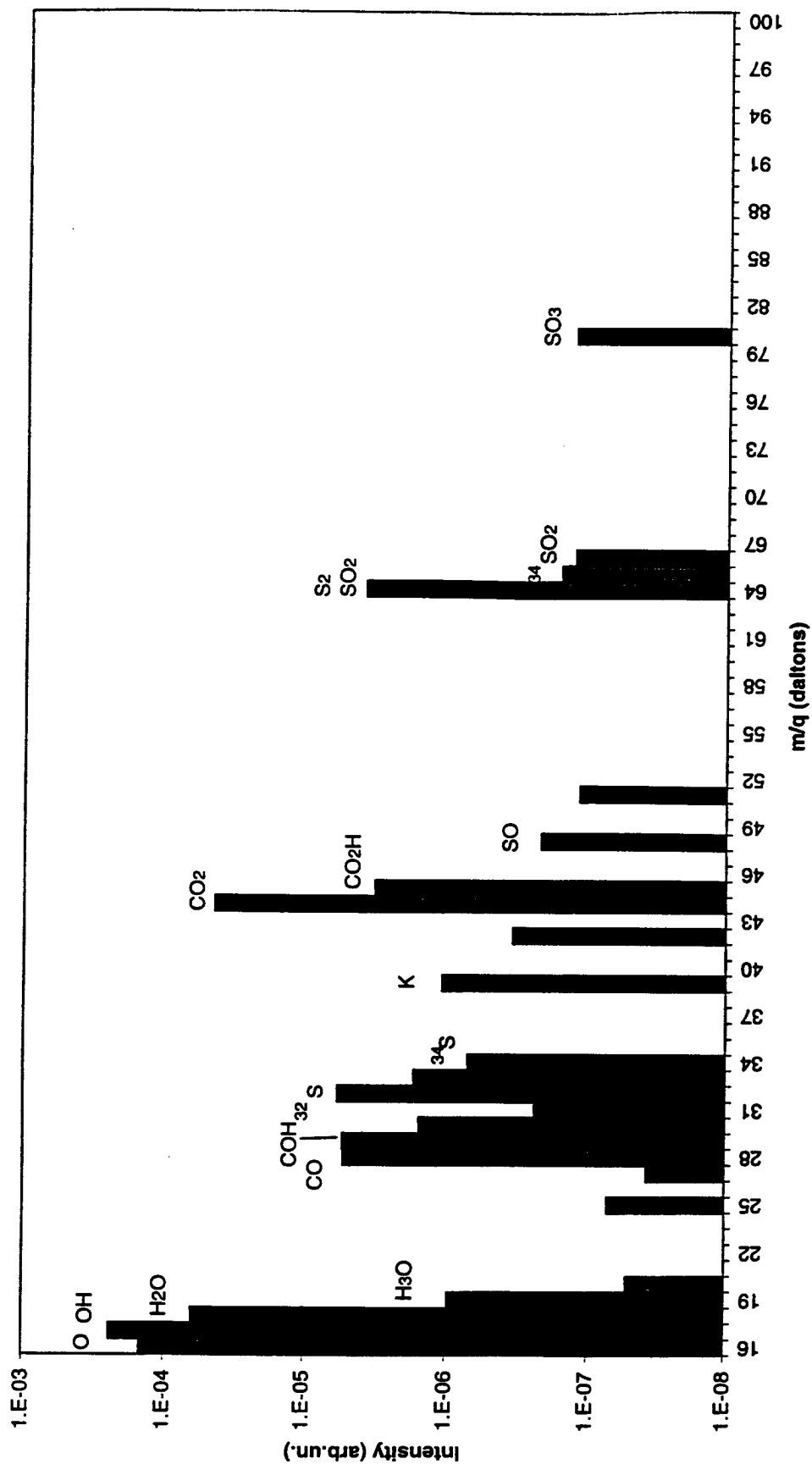


Figure 8 : Mass spectrum measured on the polysulfone. Effect of the neutrals.

Figure 7 shows the spectrum obtained by integrating the first peak of each measurement, i.e. the spectrum of products evolved from the surface under ions and UV bombardment. Figure 8 shows the spectrum of products evolved under neutrals bombardment.

Identification of the peaks corresponding to sulphured products is facilitated by the presence of the ^{34}S isotope corresponding to about 4% of ^{32}S .

In both spectra (figure 7 and 8), the emitted products (CO ; CO_2 , SO , SO_2 and SO_3) are typical of the photooxidation of sulphured polymers. However, we cannot distinct in the peak at $m/q = 64$, the part of S_2 and SO_2 even if SO_2 is more probable, resulting of the action of atomic oxygen.

Comparing the action of ions and neutral, the same products are observed and the forms of both spectra are similar. In figure 7, SO_2 and SO_3 do not appear because of difficulty to interpret the signal obtained with this mass, as it will be shown in the next paragraph.

6.1.3 Velocity spectra of different products :

Figures 9, 10, 11, 12 and 13 show the signal measured for the mass/charge ratio $m/q = 28$, 44, 48, 64 and 80.

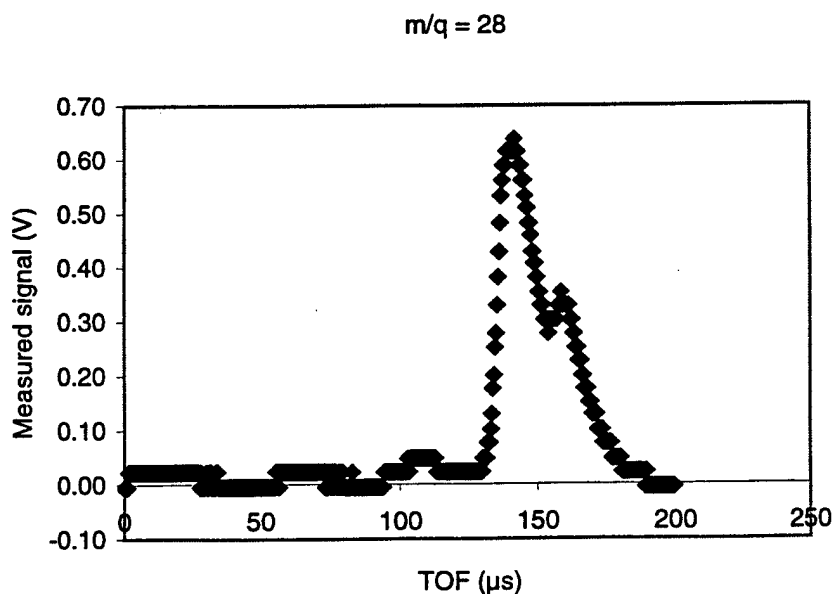


Figure 9 : Velocity spectrum measured for the masse/charge ratio $m/q = 28$

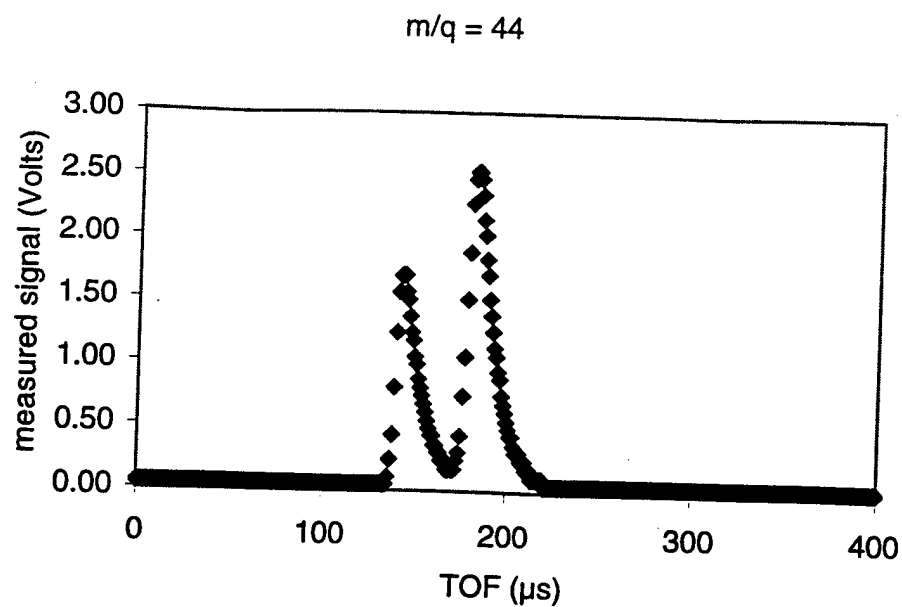


Figure 10 : Velocity spectrum measured for the masse/charge ratio $m/q = 44$

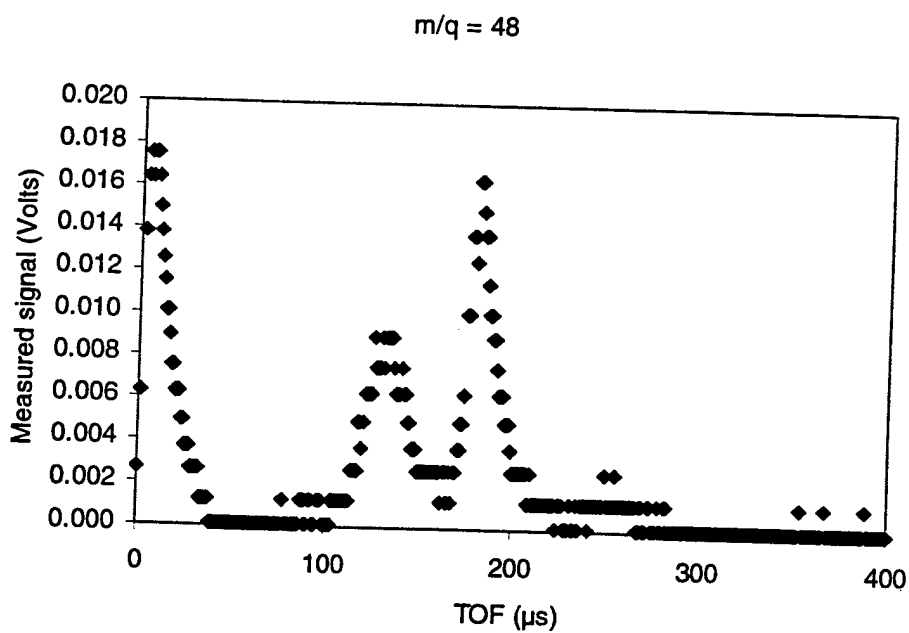


Figure 11 : Velocity spectrum measured for the masse/charge ratio $m/q = 48$

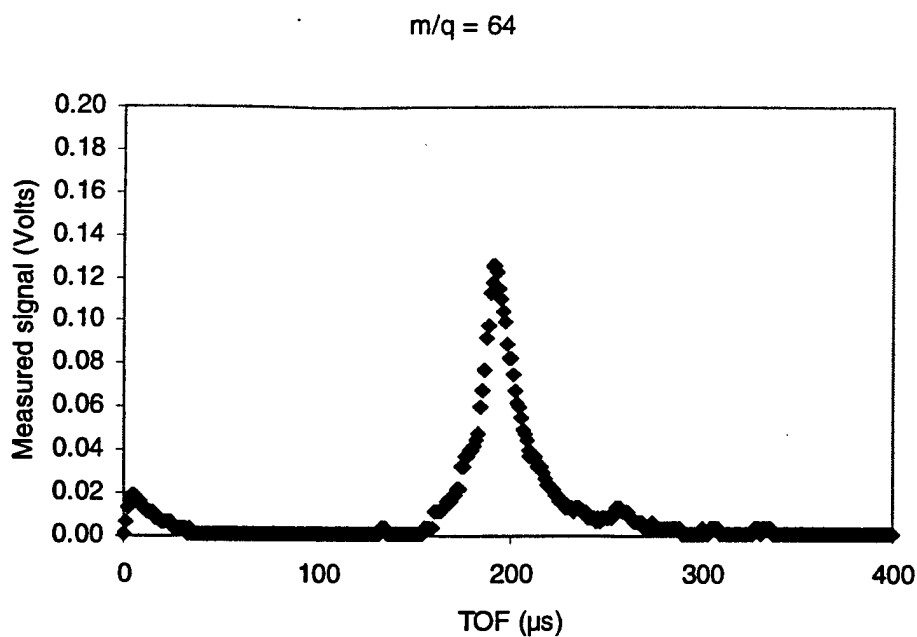


Figure 12 : Velocity spectrum measured for the masse/charge ratio $m/q = 64$

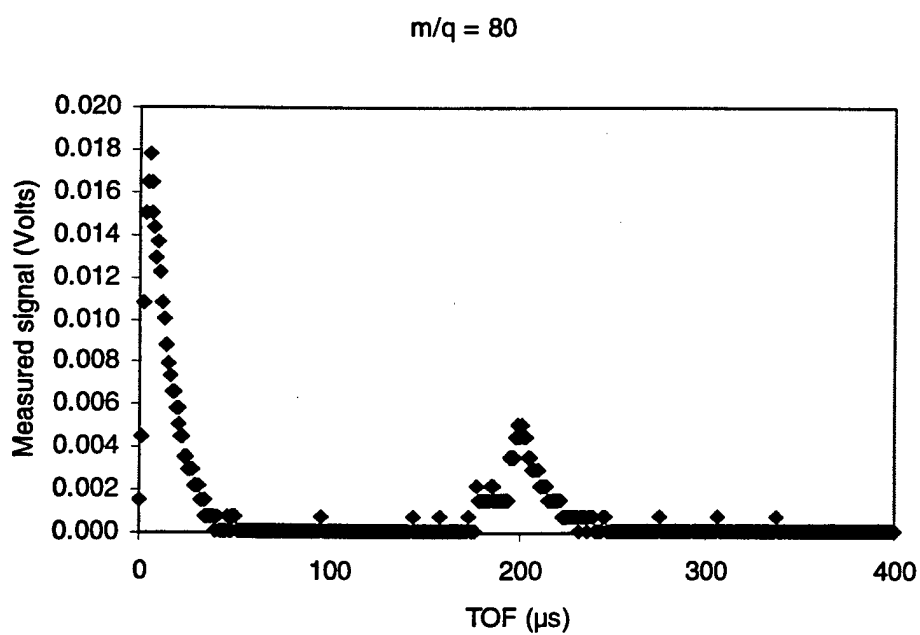


Figure 13 : Velocity spectrum measured for the masse/charge ratio $m/q = 80$

When the scale allows us to see very small signals (for $m/q = 64$ or 80 for example), we can observe the presence of a first peak at $t = 0$. This peak corresponds to a photoelectron emission on the SEM converting dynode; it is induced by the UV-VUV photons emitted during initial oxygen plasma formation within the nozzle. Although the mass spectrometer is not in the UV-VUV propagation axis, photons enter the mass spectrometer after reflections on the chamber metallic walls.

When the mass/charge ratio of the measured molecules increases, the velocity of these molecules decreases. This fact explains why the peaks on the measured signals are delayed from the first mass/charge ratio $m/q = 28$ to $m/q = 80$.

However, on the figures 11 and 12 ($m/q = 64$ and 80), it is quite difficult to interpret the measured peak since it appears around $200\mu s$. We considered that this peak was due to neutrals impact since $200\mu s$ is the time of neutrals peak appearance.

7 SAMPLES EXPOSURE :

The sample (a piece of polysulfone – 1 cm^2) was exposed with kapton samples to the raw beam of CASOAR and then to the neutral beam cleared out by removal of its charged species. The sample were weighed before and after the test and the mass loss of the kapton gave us the received fluence. This was $5.8 \cdot 10^{19}\text{ at/cm}^2$ in each case raw beam and neutral beam). The mass loss on the samples of polysulfone were very close to each other, around 0.6 mg for a sample mass of 28 mg .

This result was obtain only on one sample and one experiment but gives us an idea of the influence of ions in the erosion rate of this material and this influence is very small.

8 CONCLUSION :

This study was devoted to the characterization of products evolved from polysulfone targets under a well-known beam of atomic oxygen.

The characterization of the oxygen beam of CASOAR showed the presence of ionic particles that travel faster than neutral ones at around 13 km/s. The ionic particles participate to the ionization of the reaction products by charge transfer and allowed us to use ion optics to bring these products to the mass spectrometer to be analyzed. However, these particles are a small part of the beam (few ppm) and do not participate very perceptibly to the erosion of the samples.

Species like CO, CO₂, SO or SO₂ were been evidenced in the products evolved from the surface by the beam.

An improvement of this study could be combine or sequential exposures of atomic oxygen and UV or electrons.

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[3] Cazaubon B., Paillous A., Siffre J., Thomas R. , "Mass Spectrometry Analysis of Reaction Products of Fast Oxygen Atoms-Materials Interactions", accepted for publication in Journal of Spacecraft and Rockets.